Reformate Cleanup: The Case for Microchannel Architecture

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Objectives

The overall objective of the effort at PNNL is to apply microchannel architectures where appropriate in fuel processing systems for transportation, stationary, and portable applications to reduce size and weight, improve fuel efficiency, and enhance operation. Specific objectives for this project are focused on CO cleanup and balance of plant, including

- Demonstrating 90% conversion of CO in a single-stage water-gas shift (WGS) reactor that scales to less than three liters at full-scale (50 kWe),
- Evaluating the potential importance of microchannel architectures in reducing the size and weight and improving performance of preferential oxidation (PROX) reactors,
- Exploring the ability to improve H_2S adsorption with conventional sorbents through improved temperature control, and
- Developing compact microchannel heat exchange technology for the recovery and recycle of water in fuel processor/fuel cell systems.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- R. Thermal and Water Management

Approach

- Demonstrate a compact differential-temperature microchannel water-gas shift reactor
  - Select and characterize a high activity shift catalyst
  - Calculate the optimal temperature profile
  - Design and test a multi-channel microreactor with integrated heat exchange to demonstrate the advantage of the approach
  - Demonstrate lifetime and durability of the engineered catalyst
  - Integrate with a steam reforming fuel processor
- Investigate approaches for PROX reactor enhancements with microchannels
  - Evaluate industrial PROX catalysts for fast kinetics
  - Confirm favorable operational characteristics with effective temperature control at the 2-kWe scale

  - Investigate weight reductions through use of low-density alloys
  - Investigate transient and startup characteristics
  - Integrate with a steam reforming fuel processor
- Explore effectiveness of controlling temperature profile to enhance H_2S removal in conventional adsorbent materials
  - Quantify H_2O sorption kinetics as a function of temperature for commercial sorbent materials
  - Calculate optimal temperature profile for differential temperature adsorber
  - Construct microchannel unit and obtain experimental performance data under differential temperature conditions
  - Compare results with isothermal performance
- Integrate microchannel heat exchange and phase separation technology to recover and recycle water in fuel processor/fuel cell systems

Accomplishments

- Performed extended operation and thermal cycle testing of precious metal water-gas shift catalyst in engineered form
- Continued efforts toward demonstrating differential temperature WGS operation in a multi-channel counter-flow reactor
- Designed and built a prototype first-stage microchannel PROX reactor at the 2-kWe scale and demonstrated effective operation up to 4 kWe
- Demonstrated a multi-channel air-cooled partial condenser with integrated phase separation on a simulated cathode effluent at the 1.5-kWe scale

Future Directions

- Continue catalyst development with focus on durable engineered forms of commercial WGS catalyst
- Design, build and test a second generation differential temperature microchannel reactor
- Evolve PROX reactor concepts for higher productivity and improved thermal control
- Demonstrate differential temperature H_2S sorption
- Integrate WGS, PROX, and sulfur removal in an integrated steam reforming fuel processor
- Pursue fabrication alternatives to facilitate low cost manufacturing targeting low temperature components

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Introduction

A critical aspect of attaining size and weight objectives for on-board fuel processors is achieving rapid heat and mass transfer rates, which is made possible by microchannels. This has been demonstrated in the past for the highly endothermic steam reforming reaction in microchannel reactors having integrated heat exchange to supply the necessary heat. This project extends the effort to the areas of reformate cleanup and balance-of-plant, in order to identify other elements of a fuel processing/fuel cell system that can benefit from the microchannel architecture.

The water-gas shift (WGS) reaction is the conventional processing step after the fuel reformer to convert carbon monoxide to carbon dioxide, thereby reducing CO as a poison for PEM fuel cells while increasing hydrogen yield. The WGS reaction is exothermic, so that high temperature operation favors kinetics but equilibrium is more favorable at low temperature. The conventional approach is to operate a high temperature shift (HTS) reactor above 400°C, followed by a low temperature shift (LTS) reactor operating below 300°C to achieve the necessary conversion, with a heat exchanger in between to cool the reformate. A more optimal temperature profile could reduce the size of the shift subsystem and reduce the amount of catalyst required. The preferential oxidation (PROX) reactor is used to reduce carbon monoxide to levels that can be tolerated by PEM fuel cells by selectively oxidizing CO with air. Typically, PROX catalysts have a relatively narrow temperature window where CO conversion and selectivity are high. Microchannel approaches for integrating heat exchange within a PROX reactor offer potential improvement in PROX reactor performance.

The conventional approach for removing hydrogen sulfide, a poison for downstream catalysts and the fuel cell, from the reformate stream is adsorption using zinc oxide. H_2S adsorption also exhibits a temperature trade-off between sorption equilibrium and increased mass transfer rates, so improved localized temperature control is expected to improve performance. Finally, because fuel processors and fuel cells require water, recovery and recycle of water is necessary, and partial condensation is an appropriate topic for microchannel heat exchange as a means for achieving water balance. Each of these topics represents opportunities for applying microchannels to CO cleanup and balance-of-plant needs, which are under investigation in this project.

Approach

The general approach is a logical sequence of steps designed to demonstrate feasibility and potential benefits for overcoming programmatic technical barriers. This typically involves selecting a catalyst material from available sources through a screening process. The selected material is then characterized in an engineered form suitable for microchannel reactors through a series of tests over a range of operating conditions. A kinetic model may be developed from detailed finite element analysis of the reactor to support subsequent reactor engineering and design. The next step is to build and test a prototype microchannel reactor as a concept demonstration and to provide experimental data for scale-up and system integration. Finally, a microchannel reactor is designed and built based on integrated system specifications and tested within an integrated fuel processor to validate system performance.

Water-gas shift and hydrogen sulfide adsorption have similar temperature trade-offs that suggest performance can be enhanced by monotonically decreasing the temperature as the process proceeds. For these applications, the approach is to utilize integrated microchannel heat exchange to actively cool the reformate stream as it passes through a microchannel reactor. For example, theoretical calculations suggest the amount of water-gas shift required can be reduced by up to half with this approach. For PROX, a two-stage reactor approach is adopted with at least the first stage actively cooled to remove heat generated by the reactions and control the temperature of the catalyst within a range where high conversion and high selectivity are obtained.

Results

Water-Gas Shift Reactor – Efforts in water-gas shift microchannel reactor development have included continuing catalyst characterization, lifetime testing, and deactivation investigations, and progress has been made in demonstrating a multi-channel WGS reactor with a decreasing reaction gas temperature profile. Two new formulations of Sud-Chemie precious metal catalysts were tested as possible improvements over the PMS5 catalyst adopted by the project in FY 2002.

The 7-channel reactor shown in Figure 1 was tested in FY 2002, and the results showed significantly lower catalytic activity than found previously in single-channel testing. This catalyst was removed from the reactor, and individual catalyst pieces were tested in an isothermal single-channel reactor. Single-channel results confirmed 20 times lower activity than expected, and issues with loading the catalyst into the reactor were identified as possible causes.

A second attempt was made to demonstrate differential temperature operation in a multi-channel counter-flow microreactor, and the results are summarized in Figure 2. Most significantly, the ability to maintain the activity of the catalyst was demonstrated. In one test at 107,000 GHSV, with the feed end temperature at 375°C and the outlet end at 325°C, 79% conversion of the CO was achieved, decreasing the dry gas CO concentration from 12.4% to 2.6%. However, differential temperature performance did not provide the advantage over isothermal operation that was expected, as illustrated in Figure 2. When the reactor was operated with the feed end at 375°C and a decreasing temperature profile, greater CO conversion and a lower outlet CO concentration was achieved when compared to isothermal operation at the colder outlet temperature. However, when compared to isothermal operation at the feed temperature of 375°C, performance was diminished. Flow maldistribution between the channels in the multi-channel reactor was identified as the cause of unexpected performance. Future efforts will target improving flow distribution while also optimizing catalyst loading and reactor configuration.

Preferential Oxidation -- Commercially available catalysts were characterized in engineered form in a single-channel microreactor, including both precious metal and non-precious metal catalysts. Based on these results, a 2-stage approach was adopted, with a lower cost, non-precious metal catalyst selected for the first stage capable of achieving 97% conversion of CO from 1% to 300 ppmv with high selectivity when operated within a 20°C temperature range centered at 200°C. A precious metal catalyst is anticipated for the second stage to further reduce the CO level to 10 ppmv.

A prototype reactor was designed and built for first stage PROX at the 2-kWe scale. The reactor shown in Figure 3 has four chambers, each with separate air addition. A microchannel heat exchanger within the reactor removes the heat generated from the reaction. Quasi-isothermal conditions are maintained within the PROX catalyst by the heat exchanger and by modulating air addition to each chamber. The operational characteristics of this reactor were determined by varying the reformate flow rate, operating temperatures, O_2/CO ratios in each chamber, and inlet CO concentration (between 1-2% on a dry basis). The flow rate range corresponded to between 2 and 4.7 kWe equivalent fuel cell power output. Conversion profiles through the reactor are shown in Figure 4 for four power levels. Over 97% CO conversion was achieved at the

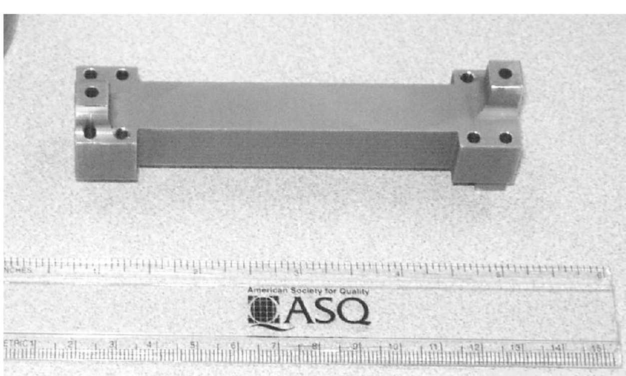

Figure 1. Seven-Channel WGS Reactor with Interleaved Counter-Current Heat Exchange Microchannels for Isothermal and Differential Temperature Operation

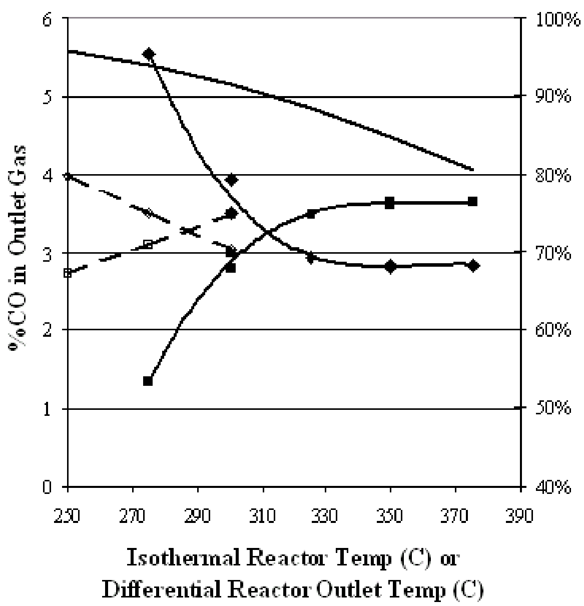

Figure 2. Comparison of Isothermal and Differential Temperature Operation with Steam Reformate Feed (12.4% CO and 14.3 CO_2, dry gas) at 100,000 GHSV and 0.65 Steam to Dry Gas Showing CO Conversion (■) and CO Concentration (□) under Isothermal Operation and CO Conversion (◆) and CO Concentration (✧) under Differential Mode with the Reformate Feed at 350°C with the Equilibrium CO Conversion Line Shown at the Top

4-kWe power level, which was twice the design objective.

Desulfurization – Development of microchannel desulfurization technology was initiated in FY 2003, and efforts to date have been focused on developing experimental and analytical capabilities to support testing. Initial studies are underway to characterize CO uptake onto zinc oxide materials as a function of temperature to support calculations of optimal temperature profile to balance kinetics and sorption equilibrium.

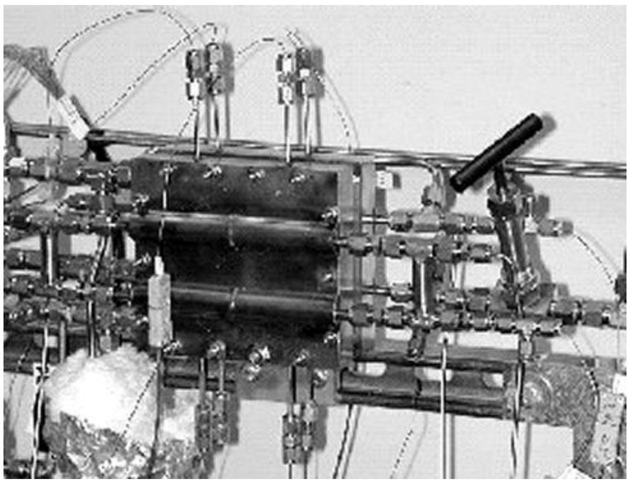

Figure 3. Prototype PROX Reactor with Microchannels for Quasi-Isothermal Operation and Multiple Compartments for Staged Air Injection

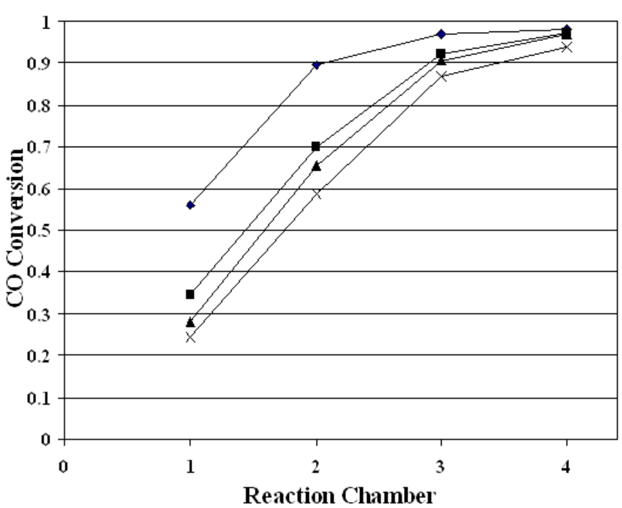

Figure 4. Carbon Monoxide Conversion Profiles through the Prototype First-Stage PROX Reactor Operated with an Overall O_2/CO Ratio of 1.0, Feed CO Concentration of 1.14% (dry), 0.3 Steam to Dry Gas Ratio, and Reformate Flow Rates Corresponding to 2 kWe (◆), 3 kWe (■), 4 kWe (▲), and 4.7 kWe (X)

Partial Condensation with Phase Separation – A prototype multi-channel partial condenser with phase separation was tested over a range of flows, water content and temperatures. The cross-flow, air-cooled device was designed to recover water from the effluent stream from the cathode of a PEM fuel cell at approximately the 1.5-kWe scale. Design conditions include hot feed at 80°C, coolant air at 30°C, and air-side pressure drop of 2.2 inches of H_2O that would require an estimated 14 W of parasitic load at full scale. The aluminum device is extremely lightweight and includes a phase separator to remove the condensate separate from the gas effluent. The device is shown in Figure 5, and the results of testing are compiled in Figure 6, including comparison to theoretical prediction. Actual performance exceeds predicted performance, and specific power exceeded 2000 Wt/kg at 74% water recovery. Water separation efficiency was 90-100%, and the coolant side pressure drop was about 4 inches of H_2O, which was about twice the design value.

Conclusions

- Although additional work remains in demonstrating 90% conversion in a single-stage water-gas shift reactor using the differential temperature microchannel reactor concept, the approach remains valid for achieving a WGS

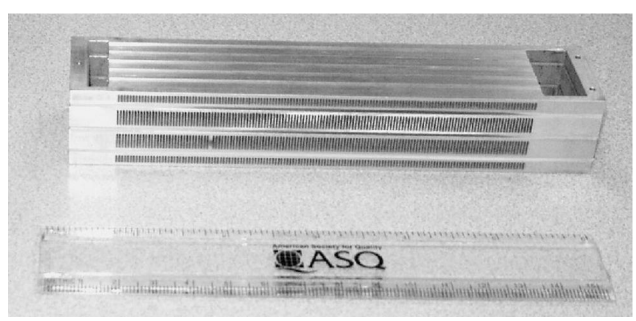

Figure 5. Aluminum Microchannel Partial Condenser Containing 3 Sets of 0.020-inch Condensing Microchannels Interleaved with Cross-Flow 0.024-inch Cooling Channels

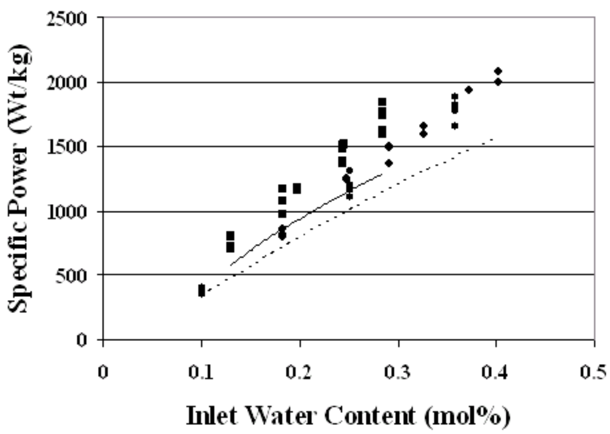

Figure 6. Specific Power versus the Water Content of the Prototype Microchannel Partial Condenser at Condensing Stream Air Flows of 32 SLPM (●) and 48 SLPM (■) with Trend Lines Shown through the Predicted Performance Values at the Same Operating Conditions that Produced the Experimental Data for Both 32 SLPM Air Flow (- - -) and 48 SLPM Air Flow (——).

reactor that is less than 3 liters at the 50-kWe scale.

- A prototype first-stage PROX having integrated microchannel heat exchange has been shown to have excellent thermal control and high productivity.
- Improving desulfurization using conventional sorbent materials is viable by optimizing thermal profiles using microchannels.
- Lightweight, high thermal conductivity metals, such as aluminum, can be used in fabricating microchannel devices having high specific power for lower temperature components, including microchannel partial condensers for water management in fuel processors and fuel cell systems.

FY 2003 Publications/Presentations

1. TeGrotenhuis, W.E., K.P. Brooks, D.L. King, R.S. Wegeng, "Optimizing the Water Gas Shift Reaction in Microchannel Reactors by Trading-Off Equilibrium and Reaction Kinetics through Temperature Management", poster presentation at the **2002 Fuel Cell Seminar**, November 18-21, Palm Spring, California.

2. TeGrotenhuis, W.E. and V.S. Stenkamp, "Testing of a Microchannel Partial Condenser and Phase Separator in Reduced Gravity", presented at **First International Conference on Microchannels and Minichannels**, April 24-25, 2003, Rochester, New York, USA (proceedings in print).